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Chemistry

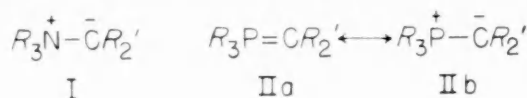
PENTAVALENT ORGANOPHOSPHORUS COMPOUNDS

By B. D. WILSON

I. Phosphorus Ylids

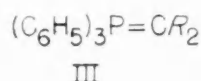
A. Introduction

Alkylidenetrialkyl- (or aryl-) phosphoranes, more commonly called *phosphorus ylids*, as a class contain almost all known pentavalent organophosphorus compounds with only carbon bonded to the phosphorus atom. The term *ylid* as applied to these compounds is somewhat of a misnomer, for in contrast to the nitrogen ylids (I), the phosphorus ylids (II) are actually a resonance hybrid between the ylene form (IIa) and the ylid form (IIb), but more closely resemble IIa than IIb. Strictly speaking,



then, these alkylidenephosphoranes should be called *ylenes* instead of ylids.

The investigations of phosphorus ylids circumscribe a broad range, but for the most part have been limited to alkylidenetriphenylphosphoranes (III) because they are the only ylids which have found synthetic use, namely, in the Wittig reaction. Consequently, this article will be limited primarily to a discussion of alkylidenetri-

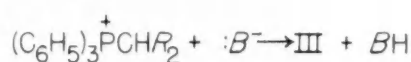


phenylphosphoranes, but it must be remembered that, with few exceptions, the statements also apply to other members of the series.

B. Methods of Preparation

Phosphorus ylids have been prepared by several methods, none of which is completely general.

1. *From Phosphonium Salts* (1).—This most nearly general preparation of ylids consists in removal of a proton from the α -carbon atom of an alkyltriphenylphosphonium salt by nucleophilic attack of a base.



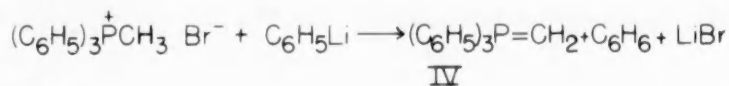
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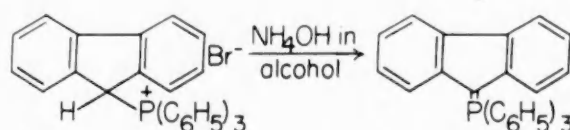
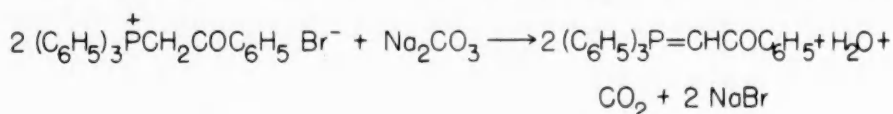
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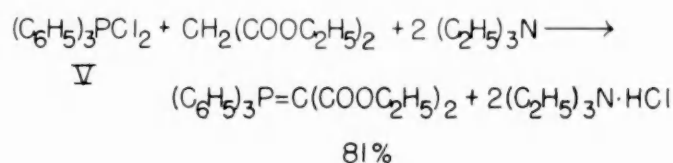
The base must be very strong for ylids which have little stabilization of the ylid form IIb (2).



A very mild base is satisfactory for many highly stabilized ones (3, 4).



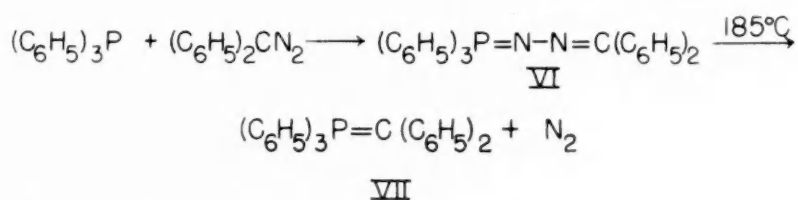
2. *From Triphenyldihalophosphoranes.*—Triphenyldichlorophosphorane (V) with reactive methylene compounds in the presence of a tertiary amine yields the corresponding ylid (5).



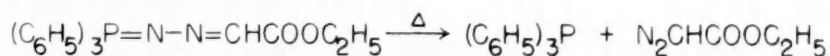
3. *From Carbenes.*—In two very recent communications (6, 7), triphenylphosphine has been found to react with dichloro- and other carbenes, yielding ylids.



4. *From Phosphazines.*—Staudinger and his co-workers (8) actually prepared the first phosphorus ylid, VII, with the discovery that pentaphenylphosphazine (VI), prepared from triphenylphosphine and diazodiphenylmethane, on heating, split out nitrogen.



In most other cases, however, Staudinger found that, on heating, the phosphazine merely gave back its components (9, 10).

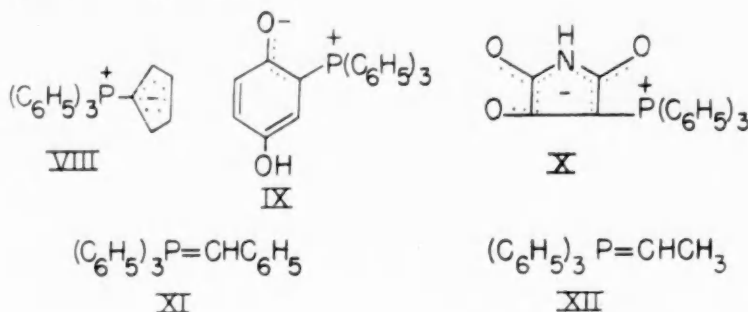


This method no longer has any practical significance, because these types of ylids are more easily reached *via* the phosphonium salt (Method 1).

C. Stability

Generally speaking, the stability of phosphorus ylids corresponds directly to the resonance stabilization afforded the separate charges of the ylid form IIb (11).

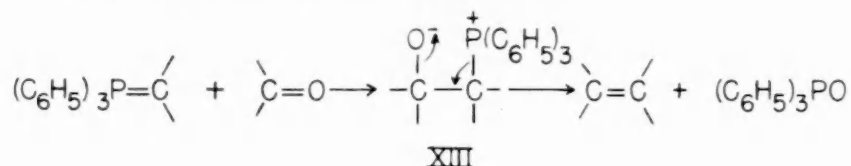
Ramirez (3, 12) has classified phosphorus ylids into three groups, based on the anion charge stabilization. Type 1 ylids have the charge incorporated into the π electron cloud of an aromatic system, e.g., VIII (11). Type 2 ylids have the charge stabilized as a part of an aromatic system, e.g., IX (13), or as a part of some other mesomeric system, e.g., X.



Any anion charge stabilization that Type 3 ylids may possess is only *via* conjugated groups, e.g., XI (2, 14) or XII (15). The stability decreases as one goes from Type 1 through Type 2 to Type 3.

D. Reactions

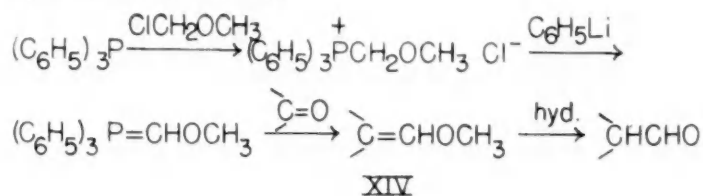
1. *The Wittig Reaction.*—The best-known reaction of phosphorus ylids was discovered by and named after Wittig (2). In this reaction, the ylid reagent reacts with a carbonyl compound, giving a net effect of exchange of the alkylidene and the oxygen groups, to yield an olefin and triphenylphosphine oxide. It is generally accepted that the mechanism involves nucleophilic attack by the ylid on the carbonyl carbon atom, with a betaine (XIII) as an intermediate.



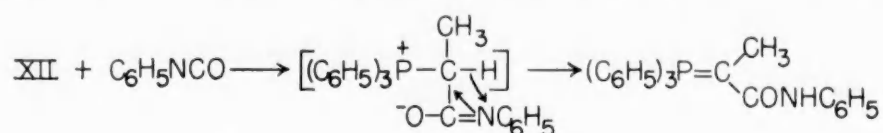
Although the reaction proceeds with almost any carbonyl compound, the nature of the ylid is severely limited, as alkylidenetriaryl- (in practice, triphenyl-) phosphoranes (III) are the only reagents used. In addition, the nature of the alkylidene moiety is important. In general, the more resonance-stabilized the anion, the less likely reaction with carbonyl compounds will occur (11). Thus, only the more reactive members of Type 3 undergo the Wittig reaction, e.g., VII will not react, whereas XI reacts only with aldehydes and very reactive ketones (e.g., Michler's ketone) (14).

In spite of these broad limitations, the Wittig reaction has been widely accepted and is used in many different areas of organic chemistry, primarily because it is much superior to previously available methods for bringing about the same conversion. Since there are several excellent review articles (16-20) on the Wittig reaction, only a few important recent applications will be mentioned.

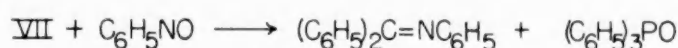
a. Aldehyde Syntheses (21, 22).



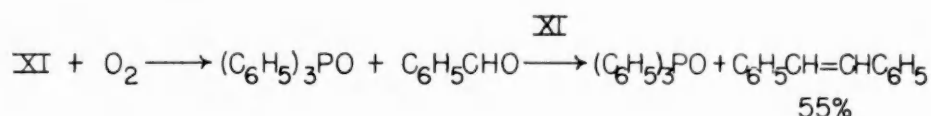
Recently, it has been observed (28) that when the ylid methylene carbon atom has a hydrogen atom, its migration to nitrogen occurs during the reaction with phenyl isocyanate, probably as the betaine intermediate. The rearrangement, instead of leading to fission of the betaine, leads to a new, more stable ylid.



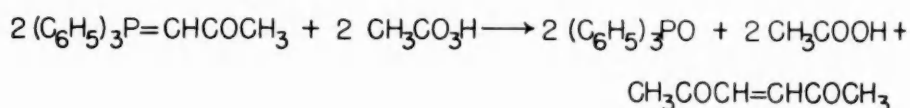
Staudinger's diphenylmethylenetriphenylphosphorane, VII, also has been shown (29) to react with nitrosobenzene.



3. *Oxidation.* Autoxidation of oxygen-sensitive ylids leads to symmetrical olefins (30).

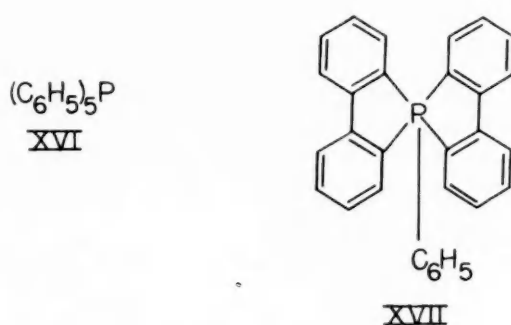


Oxidation of "weakly basic" (i.e., highly resonance-stabilized) ylids by peracetic acid also leads to symmetrical olefins (31).



II. Pentacovalent Phosphorus Compounds

Only two examples of compounds with five P-C bonds have appeared in the literature, XVI (32) and XVII (33). The method used to prepare XVII appears to be



quite general, although no further examples have yet appeared in the literature.

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